

# AP Chemistry

## Thermodynamics

- For each of the following, specify which has the higher entropy.
  - A sample of dry ice (solid  $\text{CO}_2$ ) at  $-78^\circ\text{C}$  or  $\text{CO}_2$  vapor at  $0^\circ\text{C}$ .
  - Sugar, as a solid or after dissolving in a cup of coffee.
  - A chunk of metallic sodium or a flask of argon at room temperature.
  - Two connected flasks of equal volume, one containing pure ammonia and the other pure nitrogen, or both gases mixed and occupying the flasks equally.
- In each of the following pairs, decide which compound has the higher entropy at  $298\text{K}$ :
  - $\text{NaCl}$  or  $\text{MgCl}_2$
  - $\text{Cl}_{2(g)}$  or  $\text{P}_{4(g)}$
  - $\text{CH}_3\text{NH}_2$  or  $(\text{CH}_3)_2\text{NH}$
  - $\text{Au}_{(s)}$  or  $\text{Hg}_{(l)}$
- The enthalpy of vaporization of liquid diethyl ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ , is  $26.0\text{kJ/mol}$  at the boiling point of  $35.0^\circ\text{C}$ . Calculate  $\Delta S$  at  $35.0^\circ\text{C}$  for
  - liquid to vapor
  - vapor to liquid
- Calculate the standard entropy change for each of the following reactions at  $25^\circ\text{C}$ :
  - $\text{Mg}_{(s)} + \frac{1}{2} \text{O}_{2(g)} \rightarrow \text{MgO}_{(s)}$
  - $\text{Pb}_{(s)} + \text{Cl}_{2(g)} \rightarrow \text{PbCl}_{2(s)}$
  - $2\text{ICl}_{(g)} \rightarrow \text{I}_{2(s)} + \text{Cl}_{2(g)}$
  - $\text{C}_2\text{H}_5\text{OH}_{(l)} + 3\text{O}_{2(g)} \rightarrow 2\text{CO}_{2(g)} + 3\text{H}_2\text{O}_{(l)}$
  - $\text{NaCl}_{(s)} \rightarrow \text{NaCl}_{(aq)}$
- For each of the following processes, give the algebraic sign of  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ . (No calculations are necessary. Use your common sense.)
  - The splitting of liquid water to give gaseous oxygen and hydrogen.
  - Dissolving a small amount of  $\text{NH}_4\text{Cl}$  in water (The solution becomes quite cold in the process.)
  - The explosion of dynamite (where liquid nitroglycerin gives gaseous products such as water,  $\text{CO}_2$  and others; much heat is evolved).
- Write a balanced equation depicting the formation of 1 mole of  $\text{Fe}_2\text{O}_{3(s)}$  from its elements. What is the free energy of formation of 1.00 mole of  $\text{Fe}_2\text{O}_3$ ? What is the standard free energy change when  $454\text{g}$  of  $\text{Fe}_2\text{O}_3$  is formed from its elements?
- Yeast can produce ethyl alcohol by the fermentation of glucose, the basis for the production of most alcoholic beverages.
 
$$\text{C}_6\text{H}_{12}\text{O}_{6(s)} \rightarrow 2\text{C}_2\text{H}_5\text{OH}_{(l)} + 2\text{CO}_{2(g)}$$
 Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  for the reaction. In addition to the thermodynamic values in the appendix of your text you will need the following for  $\text{C}_6\text{H}_{12}\text{O}_{6(s)}$ :  $\Delta H^\circ(\text{kJ/mol}) = -1260.0$ ;  $S^\circ(\text{J/Kmol}) = 288.9$ ;  $\Delta G^\circ(\text{kJ/mol}) = -919.2$
- Calculate  $\Delta G^\circ_{\text{rxn}}$  for each of the following reactions:
  - $4\text{NH}_{3(g)} + 5\text{O}_{2(g)} \rightarrow 4\text{NO}_{(g)} + 6\text{H}_2\text{O}_{(l)}$
  - $2\text{H}_2\text{S}_{(g)} + 3\text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)} + 2\text{SO}_{2(g)}$
  - $\text{SiCl}_{4(g)} + 2\text{Mg}_{(s)} \rightarrow 2\text{MgCl}_{2(s)} + \text{Si}_{(s)}$
- The dissociation of gaseous chlorine to  $\text{Cl}$  atoms has an equilibrium constant of  $0.106$  at  $1800\text{K}$ . Calculate the free energy change for this reaction.
 
$$\text{Cl}_{2(g)} \leftrightarrow 2\text{Cl}_{(g)}$$
- Water reacts with  $\text{SiCl}_4$  to produce  $\text{SiO}_2$  and  $\text{HCl}$ 

$$\text{SiCl}_{4(g)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{SiO}_{2(s)} + 4\text{HCl}_{(aq)}$$
  - Using the data in the appendix, calculate  $\Delta G^\circ$  for the reaction. Is the reaction predicted to be spontaneous under standard condition?
  - From  $\Delta G^\circ_{\text{rxn}}$  calculate  $K_p$ . Are products or reactants favored at  $25^\circ\text{C}$ ?



## AP Chemistry Thermodynamics (Homework Answers)

- 1 a)  $\text{O}_2$  vapor @  $0^\circ\text{C}$  entropy is always greater in gas form  
b) dissolved Sugar entropy of dissolved substance is always greater than its Solid  
c) Flask of Argon gases more disordered than solids  
d) The "mixed" flask mixed gases are always more disordered.

2. a)  $\text{MgCl}_2$  Entropy increases as the number of ions/formula unit  
b)  $\text{P}_4$  The larger the number of atoms/formula the greater the disorder  
c)  $(\text{CH}_3)_2\text{NH}$  Same reason as in b.  
d)  $\text{H}_2\text{(l)}$  Entropy is generally greater for liquids than for Solids.

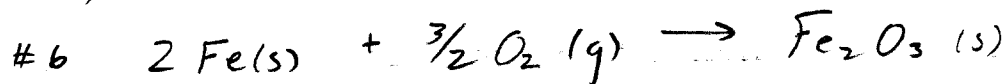
3 a)  $\Delta S$  for  $(\text{C}_2\text{H}_5)_2\text{O (l)} \rightarrow (\text{C}_2\text{H}_5)_2\text{O (g)}$   
$$\Delta S = \Delta H_{\text{vap}}/T = 26.0 \times 10^3 \text{ J/mol} / 308 \text{ K}$$
$$= \boxed{+84.4 \text{ J/Kmol}}$$

- b) for gas to liquid  $\Delta S = \boxed{-84.4 \text{ J/Kmol}}$  note the reduction in entropy from gas to liquid

#4 a  $\text{Mg (s)} + \frac{1}{2} \text{O}_2 \text{(g)} \rightarrow \text{MgO (s)}$   
$$\Delta S^\circ = 1 \cdot S^\circ \text{MgO} - \left[ 1 \cdot S^\circ \text{Mg} + \frac{1}{2} \cdot S^\circ \text{O}_2 \right]$$
$$= (1 \text{ mol})(26.94 \text{ J/Kmol}) - \left[ (1 \text{ mol})(32.68 \text{ J/Kmol}) + \left( \frac{1}{2} \text{ mol} \right)(205.14 \text{ J/Kmol}) \right] = \boxed{-108.31 \text{ J/K}}$$

- b -151.9 J/K  
c -155.89 J/K  
d -138.9 J/K  
e -42.92 J/K

#5	$\Delta H^\circ$	$\Delta S^\circ$ (more molecules) (change to gas)	$\Delta G^\circ$
a)	+	+	+
b)	+	+	-
c)	-	+	-



$$\Delta S^\circ_{\text{rxn}} = -275.87 \text{ J/K}$$

$$\Delta H^\circ_{\text{rxn}} = -824.2 \text{ kJ}$$

$$\Delta G^\circ_{\text{rxn}} = -824.2 \text{ kJ} - (298 \text{ K})(-275.87 \text{ J/K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$= \boxed{-742.0 \text{ kJ}}$$

$$454 \text{ g Fe}_2\text{O}_3 \times \frac{1 \text{ mol Fe}_2\text{O}_3}{160 \text{ g Fe}_2\text{O}_3} \times \frac{-742.0 \text{ kJ}}{1 \text{ mol Fe}_2\text{O}_3} = \boxed{-2.11 \times 10^3 \text{ kJ}}$$

#7  $\Delta H^\circ_{\text{rxn}} = \boxed{-82.4 \text{ kJ}}$

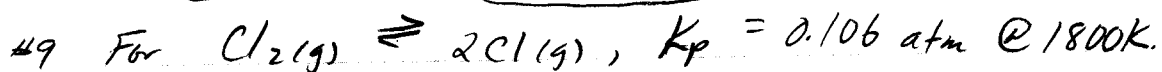
$$\Delta S^\circ_{\text{rxn}} = \boxed{460.0 \text{ J/K}}$$

$$\Delta G^\circ_{\text{rxn}} = \boxed{-219.2 \text{ kJ}}$$

#8 a)  $\Delta G^\circ_{\text{rxn}} = \boxed{-1010.8 \text{ kJ}}$

b)  $\Delta G^\circ_{\text{rxn}} = \boxed{-990.41 \text{ kJ}}$

c)  $\Delta G^\circ_{\text{rxn}} = \boxed{-566.60 \text{ kJ}}$



The free energy change is:

$$\Delta G^\circ_{\text{rxn}} = -RT \ln K_p$$

$$= -(8.314 \text{ J/mol K})(1800 \text{ K}) \ln(0.106)$$

$$= 3.36 \times 10^4 \text{ J/mol or } \boxed{33.6 \text{ kJ/mol}}$$

#10 a)  $\Delta G^\circ_{\text{rxn}} = -290.32 \text{ kJ}$  Spontaneous

b)  $\Delta G^\circ_{\text{rxn}} = -RT \ln K_p$

$$-290.32 \times 10^3 \text{ J} = -(8.314 \text{ J/mol K})(298 \text{ K}) \ln K_p$$

$$117.18 = \ln K_p$$

$$\boxed{K_p = 7.77 \times 10^{50} \text{ products are favored}}$$